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(54) METHOD OF PREPARING BENZENE AND XYLENES

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The present invention relates to methods of preparing aromatic hydrocarbons comprising benzene and xylenes.

Aromatic hydrocarbons are extensively used in different branches of industry, and benzene and xylenes comprise the most commercially important such hydrocarbons. Benzene is widely used for the manufacture of a great variety of intermediate products such as cyclohexane, ethylbenzene and cumene which in turn are useful in the production of synthetic materials such as fibres, resins, rubbers and other products. Of the xylenes, the most useful are the *p*- and *o*- isomers. These isomers are employed for the production of intermediates such as terephthalic acid and phthalic anhydride and from these acids polyester fibres, resins, varnishes, plastifying agents and other products are made.

According to the present invention there is provided a method of preparing benzene and xylenes wherein a low-boiling fraction boiling-out to a temperature of from 90 to 108°C is separated by distillation from a reforming catalysate comprising a mixture of aromatic C₆—C₁₀ hydrocarbons and non-aromatic hydrocarbons; the high-boiling fraction remaining is treated in the presence of a hydrogen-containing gas at a temperature of from 450 to 600°C under a pressure of from

10 to 60 atm on a catalyst consisting of 1 to 85%, by weight of H-mordenite, 0.1 to 10%, by weight of a hydrogenating component comprising an oxide of a metal of Group VI of the periodic system, a sulphide of such a metal, a metal of Group VIII of the periodic system or a sulphide thereof, taken either separately or in combination with each other, the balance of the catalyst being binder; the resulting liquid product comprising a mixture of aromatic hydrocarbons is separated by rectification to give benzene, toluene, total xylenes, and a mixture of C₉—C₁₁ aromatic hydrocarbons; and the toluene or the toluene along with a portion of hydrocarbons boiling above the boiling point of toluene are recycled back to the stage of catalytic treatment of the high-boiling fraction.

By using this method of preparing benzene and xylenes it is possible to increase substantially the yield of said products and to simplify their separation. Moreover, it is possible to obtain "total xylenes" substantially free from ethylbenzene thus facilitating further treatment and separation of the xylenes. In addition, the necessity of performing a separate process for isomerization of xylenes can be circumvented.

In the method of the present invention reforming catalysates of gasoline fractions comprising mixtures of aromatic C₆—C₁₀ hydrocarbons and non-aromatic hydrocarbons are used. A low-boiling fraction is distilled off from the reforming catalysate and the remaining high-boiling fraction is treated in the presence of hydrogen at an elevated temperature and under a pressure within the range of from 10 to 60 atm on a catalyst. The catalyst consists of mordenite, a hydrogenating agent, and balance binder.

According to the present invention, the low-boiling fraction, boiling out to a temperature of from 90 to 108°C, is separated and the remaining high-boiling fraction is treated at a temperature of from 450 to 600°C, using a catalyst preferably containing H-mordenite in an amount of from 1 to 85% by weight and MoO₃, WO₃, Co, Pt taken either separately or in various combinations with each

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other in an amount of from 0.1 to 10% by weight as a hydrogenating agent. The resulting liquid product is then separated by rectification to give benzene, toluene, total xylenes and a mixture of C_9 — C_{10} aromatic hydrocarbons. Certain hydrocarbons obtained from rectification of the liquid product, viz toluene or toluene along with a portion of hydrocarbons boiling above the boiling point of toluene, are recycled back to the stage of treatment of the high-boiling fraction.

The reforming catalysts are catalysts of reforming of wide gasoline fractions and containing a mixture of aromatic C_9 — C_{10} hydrocarbons and non-aromatic hydrocarbons. Such catalysts are obtained upon catalytic reforming of fractions of straight-run gasoline boiling out within the range of from 60 to 180°C, for example fractions over the ranges 85 to 180°C, 70 to 160°C, and 70 to 180°C. It is preferred that the content of aromatic hydrocarbons in the catalysts be above 60% by weight. The latter are obtained upon reforming of gasolines under severe conditions using platinum/alumina catalysts containing dopes of rhenium, iridium and other promoters. The severe reforming conditions involve a relatively low pressure and elevated temperatures, at which the typical process of reforming aimed at the production of highly-aromatized gasolines is performed.

In accordance with the method of the present invention, a low-boiling (head) fraction with the boiling end between 90 and 108°C, preferably from 100 to 106°C, is first distilled off from the starting reforming catalyst. The head fraction usually constitutes 20 to 35% by weight of the reforming catalyst, and contains mainly paraffin hydrocarbons, benzene and a minor amount of toluene. The remaining high-boiling portion of the reforming catalyst is the starting feedstock for the catalytic stage of the process, and contains toluene, aromatic C_9 , C_{10} and possibly C_{11} hydrocarbons as well as non-aromatic (paraffin) hydrocarbons. The amount of paraffin hydrocarbons in said fraction is, as a rule, below 15% by weight. This high-boiling portion of the catalyst, along with hydrogen or other hydrogen-containing gas and the recycled stream of a portion of the liquid product obtained in this process is passed, under the above-described conditions, through a catalyst bed consisting of H-mordenite, a hydrogenating component and a binder.

An important feature of the present invention is that the reaction step is performed at a temperature within the range of from 450 to 600°C in the catalyst bed. At a temperature below 450°C the liquid product contains an increased amount of paraffin C_9 — C_{11} hydrocarbons which hinders separation of xylenes by rectification. At a temperature

exceeding 600°C the stability of the catalyst is impaired.

As a result of the catalytic treatment a gas-liquid mixture is obtained. This mixture is cooled and the gas stream is separated from the liquid product. The liquid product comprising a mixture of aromatic hydrocarbons is separated by rectification to give benzene, toluene, pure total xylenes and a fraction of aromatic C_9 — C_{10} hydrocarbons. Toluene is recycled to the reaction zone as it is or along with the fraction of aromatic C_9 — C_{11} hydrocarbons, or along with a concentrate of *m*-xylene and the fraction of aromatic C_9 — C_{11} hydrocarbons. The concentrate of *m*-xylene is obtained after separation of *p*- and *o*-xylenes from the total xylenes by conventional techniques (crystallization, rectification, molecular-sieve adsorption). The concentrate of *m*-xylene is thus a mixture of aromatic C_9 hydrocarbons containing mainly *m*-xylene and also ethylbenzene and a minor amount of the non-recovered *p*- and *o*-xylenes. A portion of toluene obtained in the process may be withdrawn therefrom when required. However, recycling of toluene or at least a portion thereof is an obligatory condition of the process. It is preferred to recycle the total amount of toluene recovered from the liquid product.

The fraction of aromatic C_9 — C_{10} hydrocarbons separated by rectification contains mainly aromatic C_9 hydrocarbons. The desired products which are discharged comprise benzene and pure total xylenes. The benzene as separated from the liquid product of the process usually contains as impurities a certain amount of non-aromatic hydrocarbons. If it is necessary to obtain benzene with a purity over 99.5%, purification of the separated benzene from said impurities using conventional methods of extractive or azeotropic rectification may be effected.

A preferred method according to the present invention isolates pure benzene from two streams: from the liquid product of the process and from the low-boiling fraction of the reforming catalysts.

The purity of total xylenes recovered from the mixture of aromatic hydrocarbons by rectification can be 99.5% and above. It is known that the content of *n*-nonane, C_9 naphthenes and C_{10} paraffins in total xylenes should not exceed 0.2% by weight, since otherwise, pure *o*-xylene cannot be recovered by rectification of total xylenes. In the method according to the present invention there is substantially complete hydrocracking of these impurities and the total xylenes obtained in the process usually contain practically no C_{11} paraffins, C_9 naphthenes and *n*-nonane. Another distinctive feature of the total xylenes which can be obtained using the method according to the present invention resides in

that only an insignificant amount of ethylbenzene (1.5 to 3% by weight) is typically present therein. The total xylenes usually contain about 50% by weight of *m*-xylene and about 23 to 26% by weight of each of *o*-xylene and *p*-xylene.

The space velocity of the starting feedback with the recycle in the catalytic stage of the process is from 1 to 8 volumes per volume of the catalyst per hour.

The ratio between hydrogen-containing gas and the mixture of feedstock with recycle is varied from 600 to 2,000 nl/l.

The hydrogen-containing gas is, as a rule, recycled in the process to maintain the concentration of hydrogen therein at at least 50% by volume. The required concentration is ensured for example by adding an appropriate amount of fresh hydrogen. The gaseous products consist of paraffin C_1 — C_4 hydrocarbons; the yield of C_2 — C_4 hydrocarbons is as high as 8—10 times of the yield of methane.

The catalyst employed in the method according to the present invention consists of 1 to 85% by weight of H-mordenite, 0.1 to 10% by weight of hydrogenating agent, the balance being constituted by a binder.

H-mordenite is a crystalline aluminosilicate of cubic structure having an inlet port diameter of from 6 to 10 Å and a molar ratio of SiO_2/Al_2O_3 of 10 or over, generally from 10 to 30.

The above-indicated wide range of mordenite content permitted in the catalyst is explained by the different activities depending on the molar ratio of SiO_2/Al_2O_3 . Thus, common H-mordenite having a molar ratio of 10 to 12 is substantially less active as compared to a dealuminated mordenite having a high molar ratio of SiO_2/Al_2O_3 . For this reason, it will usually be found necessary to use more common mordenite in the catalyst than the dealuminated one. Increasing the content of mordenite above the indicated upper limit is inefficient, since it does not result in a higher activity of the catalyst and even lowers its mechanical strength. A content of mordenite below 1% by weight in the catalyst results in a lowering of the activity in the process below a critical level.

The hydrogenating components in the catalyst used in methods according to the present invention is based on metals of Group VI and Group VIII of the periodic system, preferably Mo, W, Co, Pt. They may be present in the catalyst in different forms: the Group VI metals—in the oxide form (MoO_3 , WO_3) or sulphide form; Group VIII metals—in the elemental or sulphide form. It is especially advantageous to use Mo in oxide or sulphide form, optionally in combination with other of the above-mentioned components. When MoO_3 is used, its amount in the catalyst might constitute several per cent, whereas in

the case of platinum the amount might constitute decimal fractions of a per cent.

In formulating a content of the hydrogenating components of from 0.1 to 10% by weight, the Group VIII metals are taken as calculated for the elemental condition, and the Group VI metals are calculated for the trioxide.

The catalyst composition may include H—M-mordenite, where M is at least one element of the rare-earth and alkali-earth metals such as Ca, Mg, Ce, La, or commercial mixtures of lanthanides. Such elements are introduced into the mordenite structure using ion-exchange methods; in doing so, the maximal amount of the elements should not exceed 50% of the theoretically possible degree of substitution of hydrogen cations in H-mordenite.

The binder (matrix) comprises a material imparting the required mechanical strength to the catalyst. The binder can be made of amorphous aluminosilicate, silica gel, or alumina. It is preferred to employ alumina as the binder.

The catalyst for the process can be prepared in a conventional manner characteristic of the preparation of zeolite catalysts with a binder. The usual starting Na-mordenite is converted to the H-form by treating it with an acid such as hydrochloric acid. Another method involves treatment of Na-mordenite with solutions of ammonium salts such as ammonium chloride. In this case, NH_4 -mordenite is formed which is converted to H-mordenite upon calcination. The catalyst is prepared by intermixing a paste of aluminium hydroxide with a finely-divided powder of H-mordenite or NH_4 -mordenite and with a solution of a compound of the hydrogenating component such as ammonium molybdate. After the production of a uniform plastic mass, the latter is moulded by extrusion; the resulting extrudates are dried at a temperature within the range of from 50 to 130°C and calcined in the air current.

The hydrogenating component can be also introduced by impregnating the calcined composition of H-mordenite and a binder.

When use is made of H—M-mordenite, then alkali-earth and rare-earth metals are incorporated by way of ion-exchange. Usually NH_4 -mordenite is employed for such ion-exchange.

Another method of preparation of the catalyst resides in the introduction of mordenite into a hydrosol alumina, followed by the formation of gel beads in an oil medium. Generally, the catalyst has the form of extrudates, tablets, beads or irregular-shape granules.

To reduce excess activity, the calcined catalyst is treated as a rule, with sulphur or sulphur compounds (hydrogen sulphide, sulphur-organic compounds) in a stream of

hydrogen or in a stream of hydrogen and the feedstock at a temperature within the range of from 300 to 450°C.

5 The method according to the present invention need not be technologically difficult and can be performed in the following manner.

10 In a preferred method, a reforming catalysate is fed into a rectification column, wherein the low-boiling portion of the catalysate is distilled off. The high-boiling portion of the catalysate serving as a starting feedstock for the catalytic stage of the process is discharged from the column bottom. In 15 some cases, where a reforming catalysate contains, besides aromatic C_6 — C_{10} hydrocarbons, also aromatic C_{11} + hydrocarbons, it is advisable additionally to separate the high-boiling fraction from a heavy residue containing 20 mainly aromatic C_{11} + hydrocarbons since this causes cooking of the catalyst. In this case the high-boiling fraction is fed into a second column, wherein it is distilled and discharged from the column top, whereas the heavy residue is withdrawn from the bottom. 25 The high-boiling fraction of the catalysate containing aromatic C_7 — C_{10} hydrocarbons is then delivered into the reaction unit of the process.

30 The process according to the present invention is exothermal. It can be effected in a reactor unit consisting of a number of series-connected reactors or in a shelf-type reactor, wherein the catalyst is placed on a number of 35 shelves. In between the reactors or shelves the reaction mixture is cooled by removing excessive heat. Cooling is performed by admission of cold hydrogen and/or a portion of the feedstock. The feedstock for the catalytic stage and a portion of the liquid product of 40 the process to be recycled are evaporated in heat-exchangers, mixed with the recycled hydrogen-containing gas and fresh hydrogen-containing gas (typically it is the hydrogen-containing gas from the catalytic reforming 45 process).

50 The mixture is heated in a furnace to the required temperature. The heated mixture is passed through a cascade of series-mounted reactors or a shelf-type reactor. At the outlet the mixture is cooled in heat-exchangers, condensed and delivered to a gas-separator unit, wherein the gaseous phase is separated from 55 the liquid one. The gaseous phase contains hydrogen and gaseous hydrocarbons. To reduce the supply rate of fresh hydrogen, the recycled hydrogen-containing gas is usually purified from the gaseous hydrocarbons by means of absorption. The liquid product of 60 the process is further delivered from the gas-separator unit into a stabilization column, wherein dissolved light hydrocarbons C_1 — C_4

are separated from the liquid product. The stable liquid product is then passed into a number of rectification columns, wherein successively separated are: benzene fraction, 65 toluene, total xylenes and aromatic C_6 — C_{10} hydrocarbons. Toluene is recycled into the process, either separately or along with aromatic C_9 — C_{10} hydrocarbons. In the case 70 where a concentrate of *m*-xylene is recycled along with toluene and aromatic C_9 — C_{10} hydrocarbons, *p* and *o*-xylenes are first separated by conventional methods from total 75 xylenes in special units. *O*-xylene is usually recovered by rectification and *p*-xylene by crystallization or molecular-sieve adsorption. The *m*-xylene concentrate remaining after separation of *p*- and *o*-xylenes contains a 80 certain amount of ethylbenzene and a residual portion of *p*- and *o*-xylenes.

Pure benzene from the benzene fraction produced in the process can be obtained by conventional methods of azeotropic or extractive distillation. In azeotropic distillation, the azeotrope-forming agent is generally acetone; 85 in the extractive distillation of benzene use is made of conventional solvents such as *N*-methylpyrrolidone or *N*-formylmorpholine.

90 If the reforming catalysate employed in the process contains a substantial amount of benzene which is present in the low-boiling fraction, it is economically efficient to recover pure benzene from that fraction as well. Benzene isolation in this case may comprise 95 intermixing of the benzene fraction from the process with the low-boiling fraction of the reforming catalysate and subsequent recovery of pure benzene from this mixture by means of extraction with selective solvents. Selective 100 solvents for the extraction such as glycols, sulpholane or *N*-methylpyrrolidone may be used.

The total xylenes produced by rectification of the liquid product are usually sufficiently 105 pure to be used in other processes without any additional purification.

For a further understanding of the present invention some specific Examples are given 110 hereinbelow by way of illustration.

Example 1.

A catalysate of reforming of a fraction of straight-run gasoline containing 72% of aromatic C_6 — C_{10} hydrocarbons is separated, by rectification, into a low-boiling fraction with 115 the boiling end of 105°C and a high-boiling (bottoms) fraction.

The yields of the low-boiling and high-boiling fractions are 28 and 72% by weight respectively as calculated for the reforming 120 catalysate.

The low-boiling fraction has the following composition, per cent by weight:

non-aromatic hydrocarbons	77.0
benzene	19.3
toluene	3.7

The high-boiling fraction has the following composition, per cent by weight:

non-aromatic hydrocarbons	8.9
toluene	22.6
C ₈ -aromatics	34.8
C ₉ -aromatics	30.5
C ₁₀ -aromatics	3.2

benzene	13.0
toluene	37.0
xylenes	29.2
C ₉ -C ₁₀ -aromatics	7.8
C ₅ -C ₉ non-aromatics	1.0
C ₉ non-aromatic	0.1
n-nonane	0.02

The gaseous products have the following composition, per cent by weight

hydrogen	9.3
methane	9.2
ethane	57.1
propane	17.9
butanes	6.5

- 5 As the starting feedstock for the reaction stage use is made of the high-boiling fraction of the reforming catalysate. A catalyst of the following composition, per cent by weight is used: MoO₃ 6.9; H-mordenite (SiO₂/Al₂O₃ = 12) 69.8; alumina 23.3. Catalyst extrudates are prepared in a conventional way and have the following dimensions: length 4 mm, diameter 3 mm. Their bulk weight is 0.5 g/cm³.
 10 The process run is performed in a direct-flow apparatus with circulation of a hydrogen-containing gas. The temperature in the catalyst bed is varied within the range of from 500 to 510°C; the pressure is 35 atm; the space velocity of the feed supply (along with the recycle) is 2 hr⁻¹; the circulation ratio of the gas is 1,800 nl/l of the feed and recycle; the supply rate of fresh hydrogen is 200 nl/l of the feed and recycle; the content of hydrogen in the circulated gas is 73% by volume.
 15 The catalyst is previously sulphidized with dimethylsulphide by adding the latter to the starting feedstock at a temperature of from 380 to 400°C under a pressure of 35 atm, whereafter the temperature is brought to 500—510°C.
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- 35 Toluene is added to the fresh feedstock until the yield of toluene, as calculated for the starting feed, becomes equal to the amount of toluene added to the fresh feedstock. Such stationary conditions of the process are achieved at a ratio of the fresh feedstock to the recycled toluene of 0.63 and 0.37 part by weight respectively, where the total is assumed to be equal to 1. Under these conditions, the yield of liquid product C₅⁺ as calculated for the mixture of fresh feedstock with the recycle, is 88.0% by weight.
 40 The liquid product C₅⁺ includes, in per cent by weight:

Benzene with the purity of 95.5% is isolated by rectification of the catalysate along with toluene, total xylenes, and a fraction boiling above the boiling point of toluene (C₉—C₁₀ aromatic hydrocarbons). By continuously supplying toluene, as a recycle, to the catalytic zone, there is produced as calculated for 100% of a fresh high-boiling fraction of the catalysate):

benzene	21.5%*
total xylenes	46.4%
C ₉ -C ₁₀ -aromatics	12.5%
*20.5% calculated for pure benzene	

Benzene formed in the process is mixed with the low-boiling fraction of the reforming catalysate and pure benzene is isolated from the mixture by extraction with a selective solvent (diethylene glycol).

There is obtained, as calculated for the starting, reforming catalysate, 19.8% of benzene and 33.3% by weight of total xylenes.

The total xylenes recovered by rectification from the liquid products of the process have a purity of 99.6% by weight and the following isomeric composition, per cent by weight:

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ethylbenzene	2.0
<i>p</i> -xylene	22.0
<i>o</i> -xylene	26.4
<i>m</i> -xylene	49.6

These results remain practically unchanged during 400 hours of catalyst operation.

Example 2.

- 5 The process conditions, catalyst and composition of the starting stock are the same as in the foregoing Example 1. Toluene along with aromatic C₉—C₁₀ hydrocarbons is recycled. The experimentally determined ratio of the fresh feedstock and recycle at the reactor inlet is:

fresh feedstock	0.55
toluene	0.315
C ₉ —C ₁₀ -aromatics	0.135
Total:	1.0

- 15 The yield of the liquid product as calculated for the mixture of the feedstock and recycle, is 88.0% by weight including:

benzene	9.5
toluene	31.5
total xylene	32.8
C ₉ —C ₁₀ -aromatics	13.5
C ₈ —C ₉ -non-aromatics	0.7
C ₉ -non-aromatics	0.1
<i>n</i> -nonane	0.02

The gaseous products have the following composition, per cent by weight:

hydrogen	8.4
methane	9.5
ethane	59.4
propane	16.3
butanes	6.4

The liquid product is separated by rectification to: benzene, toluene, total xylenes, aromatic C₉—C₁₀ hydrocarbons. Toluene and a fraction boiling at a temperature above the boiling point of xylenes is recycled to the process in the above-mentioned ratio to the fresh feedstock. The yield of benzene and total xylenes, as calculated for the fresh feedstock (high-boiling fraction of the reforming catalysate), is 17.3 and 59.6% by weight respectively.

The total xylenes have the following composition, per cent by weight:

ethylbenzene	1.6
<i>p</i> -xylene	22.6
<i>o</i> -xylene	25.4
<i>m</i> -xylene	50.4

Taking into account separation of benzene from the head fraction of the reforming catalysate, the yield of benzene is 17.8% by weight and that of total xylenes is 42.8% by weight as calculated for 100% of the catalysate.

Example 3.

This Example illustrates the possibility of carrying out under the above-mentioned conditions along with other reactions, the reaction of isomerization of xylenes.

Use is made of a catalysate of reforming of a straight-run gasoline (85—180°C), wherefrom a light fraction is first distilled boiling out up to 103°C. The high-boiling fraction has the following hydrocarbons composition, per cent by weight:

non-aromatic hydrocarbons	9.2
toluene	27.3
C ₈ -aromatics	46.0
C ₉ -aromatics	15.6
C ₁₀ -aromatics	1.9

The catalyst employed contains, in percent by weight: MoO₃, 5.0; Co, 1.0; H-mordenite, 47; alumina, 47. The conditions are the same as in Example 1 hereinbefore, except that the space velocity of supply of the feedstock and recycle is 3 hr⁻¹ and the content of hydrogen in the recycled gas is 67% by volume. Toluene, *m*-xylene (with ethylbenzene impurity and the fraction of aromatic hydro-

carbons boiling at a temperature above the boiling point of xylenes are recycled in combination. The experimentally determined ratio between the fresh feedstock and recycle is:

fresh feedstock	0.33
toluene	0.33
<i>m</i> -xylene	0.18*
C ₉ -C ₁₀ -aromatics	0.16
Total:	1.00

* 0.17 *m*-xylene and 0.01 ethylbenzene

The yield of liquid product C₈⁺, as calculated for the mixture supplied, is 93.2% by weight including:

benzene	7.4
toluene	33.0
<i>o</i> -xylene	9.5
<i>p</i> -xylene	8.5
<i>m</i> -xylene with ethylbenzene	18.0
C ₉ -C ₁₀ -aromatics	16.0
C ₈ -C ₉ -non-aromatics	0.8

- 10 The amount of non-aromatic C₈ hydrocarbons in the liquid product is 0.08% by weight including 0.01% by weight of *n*-nonane. Taking into account the continuous separation of *p*- and *o*-xylenes from the total xylenes produced in the process and the recycling of toluene along with the concentrate of *m*-xylene and fraction of aromatic C₉-C₁₁ hydrocarbons, there is obtained as calculated for the high-boiling fraction of the reforming catalyst, in per cent by weight:

benzene	22.4
<i>o</i> -xylene	28.6
<i>p</i> -xylene	25.7

Example 4.

This Example illustrates the minimal and maximal temperatures at which the carrying out of the process is still tolerable.

The starting feedstock, catalyst and process

conditions are the same as in the foregoing Example 1, except that the temperature in the catalyst bed is maintained at 450°C. With the process being conducted with the use of a fresh feedstock, the yield of the liquid product is 89% by weight, including:

benzene	7.3
toluene	25.7
total xylenes	33.1
C ₉ -C ₁₀ -aromatics	15.8
C ₈ -C ₁₀ -non-aromatics	7.1

The content of non-aromatic C₈ hydrocarbons in the catalyst is 0.29% by weight including 0.05% by weight of *n*-nonane; the content of *i*-C₁₀ is 0.06% by weight. With the above-indicated amount of the non-aromatic hydrocarbons, separation of pure total xylenes by rectification is rather difficult.

When the process is conducted under the same conditions, except that the catalyst bed temperature is varied within the range of from 590 to 600°C, the catalyst operation is not as stable as required. After only 70 hours of operation the content of C₈ paraffin hydrocarbons is about 0.3% by weight, including 0.06% by weight of *n*-nonane.

Example 5.

Use is made of a catalyst of reforming of a straight-run gasoline (85-180°C) fraction containing 63% by weight of aromatic hydrocarbons. After distilling off the low-boiling fraction boiling out up to 120°C, a high-boiling fraction (68.5% by weight of the catalyst) is obtained having the following composition, in per cent by weight:

non-aromatics	13.5
toluene	20.5
C ₈ -aromatics	33.2
C ₉ -aromatics	29.2
C ₁₀ -aromatics	3.6

Use is made of a catalyst containing, in per cent by weight: MoO₃, 7.5; H-mordenite (SiO₂/Al₂O₃=20), 2.5; alumina, 90.0.

The high-boiling fraction is used with recycle of toluene and aromatic C₈-C₁₁ hydrocarbons. The run is conducted at a temperature of 480°C, space velocity of the feedstock and recycle supply of 2 hr⁻¹, circulation ratio

of the gas of 1,200 nl/l of the feed and recycle and fresh hydrogen supply rate of 300 nl/l of the feed and recycle. The content of hydrogen in the recycled gas is 62% by volume. The mixture of feedstock and recycle at the reactor inlet contains 0.555 part by weight of the fresh feedstock, 0.325 part by weight of toluene and 0.12 part by weight of aromatic C₉-C₁₀ hydrocarbons, the total being assumed as 1.

The yield of liquid C₅⁺ product is 85.4% by weight including:

benzene	8.2
toluene	32.5
total xylenes	29.7
aromatic C ₉ -C ₁₀ hydrocarbons	12.0
non-aromatic C ₅ -C ₉ hydrocarbons	3.0

The content of non-aromatic C₉ hydrocarbons is 0.2% by weight including 0.03% by weight of *n*-nonane.

Example 6.

This Example illustrates the minimal content of H-mordenite in the catalyst.

Use is made of a catalyst containing, in per cent by weight: MoO₃, 7.5; H-mordenite (SiO₂/Al₂O₃=20), 1; alumina, 91.5.

The process conditions, feedstock and proportions of the fresh feedstock, toluene and aromatic C₉-C₁₀ hydrocarbons at the reactor inlet are the same as in the foregoing Example 5. The liquid product yield is 88.9% by weight including:

benzene	7.1
toluene	34.3
xylenes	30.2
C ₉ -C ₁₀ -aromatics	13.2
C ₅ -C ₉ -non-aromatics	4.1

The content of non-aromatic C₉ hydrocarbons is 0.28% by weight including 0.06% by weight of *n*-nonane.

The results of this Example show that the content of C₉ non-aromatic hydrocarbons, especially of *n*-nonane, is at the extreme of the tolerable limit for separation of the total xylenes by rectification. Furthermore, toluene and aromatic C₉-C₁₀ hydrocarbons are formed in an amount exceeding the amount thereof added to the fresh feedstock, i.e. a

higher ratio between the recycle and feed-stock is required.

Example 7.

The feedstock used is a high-boiling fraction of the reforming catalysate as described in Example 1 hereinbefore.

The catalyst employed consists of the following components, in per cent by weight: Pt (platinum), 0.25; H-mordenite (SiO₂/Al₂O₃=12), 75; the balance being alumina. The run is conducted at the temperature of from 480 to 490°C under a pressure of 25 atm, circulation ratio of the hydrogen-containing gas of 1,200 nl/l of the feed and recycle (the content of hydrogen is 65% by volume), supply rate of fresh hydrogen of 200 nl/l of the feed and recycle.

The experiment is conducted with toluene recycle: 0.62 part by weight of fresh feedstock and 0.38 part by weight of toluene. At the space rate of the mixture of 2 hr⁻¹ the liquid product yield is 88.4% by weight including:

benzene	11.3
toluene	38.0
xylenes	27.8
aromatic C ₉ -C ₁₀ hydrocarbons	10.3
non-aromatic C ₉ -C ₁₀ hydrocarbons	1.0

The content of C₉ non-aromatics in the liquid product is 0.15% by weight including 0.03% by weight of *n*-nonane.

Example 8.

Use is made of a catalyst containing, in per cent by weight: MoO₃, 5.0; Ni, 1.0; H-Cl-mordenite, 69; alumina 25. The Ce (cerium) content in the mordenite is 3.2% by weight which corresponds to a degree of substitution of the hydrogen ions of about 22%. A high-boiling fraction of the reforming catalysate is employed, the fraction composition being the same as in Example 1 hereinbefore. The run is performed with toluene recycle at a temperature of from 500 to 510°C under the pressure of 35 atm, circulation ratio of the gas of 1,200 nl/l of the feed and recycle and the supply rate of fresh hydrogen of 200 nl/l of the feed and recycle. The content of hydrogen in the recycled gas is 60% by volume.

Proportions of the fresh feedstock and toluene are 0.65 and 0.35 part by weight respectively. At the space rate of the mixture of 1.5 hr⁻¹, the liquid product yield is 87.8% by weight including:

benzene	12.1
toluene	35.0
xylene	29.1
aromatic C ₉ -C ₁₀ hydrocarbons	10.8
non-aromatic C ₉ -C ₁₀ hydrocarbons	0.8

The content of *n*-nonane in the products is 0.03% by weight.

Example 9.

5 A catalyst is used containing, in per cent by weight; MoO₃, 5.0; WO₃, 0.5; H—Carmordenite, 70; alumina, 24.5. The Ca content in the mordenite is 1.44% by weight which is equivalent to a degree of substitution of the hydrogen ions of about 16%. The feedstock of Example 1 is used. Recycle of toluene (0.35 part by weight of toluene and 0.65 part by weight of fresh feedstock) is carried out. The temperature is from 530 to 540°C under the pressure of 50 atm, space rate of supply of the feed and recycle of 1.5 hr⁻¹; circulation of the gas of 1,000 nl/l of the feed and recycle, fresh hydrogen supply rate of 200 nl/l of the feed and recycle. The content of hydrogen in the circulated gas is 60% by volume. The liquid product yield is 84.5% by weight including:

benzene	12.8
toluene	35.0
total xylenes	27.2
aromatic C ₉ -C ₁₀ hydrocarbons	8.8
non-aromatic C ₉ -C ₁₀ hydrocarbons	0.7

25 The content of C₉ non-aromatics is 0.14% by weight, including 0.02% by weight of *n*-nonane.

30 As can be seen from the Examples, the method according to the present invention permits an exhaustive hydrocracking of paraffin hydrocarbons forming azeotropic mixtures with aromatic hydrocarbons, whereby separation of benzene and xylenes becomes simplified. A complex combination of chemical reactions involving transformation of aromatic hydrocarbons results, in the end, in complete conversion to valuable products, i.e. benzene and xylenes. The method according to the present invention makes it possible to balance 40 a great number of reactions (dealkylation, disproportionation, transalkylation, isomerization of aromatic hydrocarbons; hydrocracking of non-aromatic hydrocarbons) and to inhibit

undesirable decomposition reactions of the aromatic ring.

The method according to the present invention makes it possible to increase the yield of benzene by 3—4 times and that of xylenes by 1.2 to 2 times, as compared to the content of these hydrocarbons in the reforming catalysate. Separation of these products is also substantially simplified. 50

Total xylenes prepared by the exemplified methods according to the present invention have a higher quality than those obtained from catalytic reforming and extraction. They contain an insignificant (1 to 3% by weight) amount of ethylbenzene and, hence, a greater amount of xylenes thus facilitating their subsequent separation and isomerization. 55

Furthermore, one of the preferred methods according to the present invention does not require any additional plant for isomerization of *m*-xylene, since after separation of *p*- and *o*-xylenes, *m*-xylene is recycled back into the process. 60

Therefore, the method according to the present invention makes it possible to simultaneously solve a series of different problems which hitherto have been solved through the use of a whole number of individual processes (extraction, dealkylation, disproportionation, transalkylation, isomerization of aromatic hydrocarbons). 65

An important feature of methods according to the present invention resides also in that they enable one to avoid separate reforming of narrow and wide gasoline fractions in order to produce aromatic hydrocarbons and a high-octane component. The invention makes it possible to obtain both types of products in a single high-capacity plant of catalytic reforming so that a portion of the catalyst employed at this plant could be treated according to the method of the present invention. 70

WHAT WE CLAIM IS:—

1. A method of preparing benzene and xylenes wherein a low-boiling fraction boiling out to a temperature of from 90 to 108°C is separated by distillation from a reforming catalysate comprising a mixture of aromatic C₉-C₁₀ hydrocarbons and non-aromatic hydrocarbons; the high-boiling fraction remaining is treated in the presence of a hydrogen-containing gas at a temperature of from 450 to 600°C under a pressure of from 10 to 60 atm on a catalyst consisting of 1 to 85% by weight of H-mordenite, 0.1 to 10% by weight of a hydrogenating component comprising an oxide of a metal of Group VI of the periodic system, a sulphide of such a metal, a metal of Group VIII of the periodic system or a sulphide thereof, taken either separately or in combinations with each other, the balance of the catalyst being binder; the resulting liquid product comprising a mixture 90

- of aromatic hydrocarbons is separated by rectification to give benzene, toluene, total xylenes, and a mixture of C_6 — C_{10} aromatic hydrocarbons; and the toluene or the toluene along with a portion of hydrocarbons boiling above the boiling point of toluene are recycled back to the stage of catalytic treatment of the high-boiling fraction.
2. A method according to Claim 1, wherein toluene with aromatic C_6 — C_{10} hydrocarbons is recycled to the stage of catalytic treatment of the high-boiling fraction.
3. A method according to Claim 1 or 2, wherein *o*- and *p*- xylenes are recovered from the total xylenes.
4. A method according to Claim 3, wherein toluene with aromatic C_6 — C_{10} hydrocarbons and a concentrate of *m*-xylene remaining after separation of *o*- and *p*- xylenes from the total xylenes is recycled to the stage of catalytic treatment of the high-boiling fraction.
5. A method according to any one of Claims 1 to 4, wherein the space velocity of the starting feed with the recycle supplied to the stage of catalytic treatment of the high-boiling fraction is within the range of from 1 to 8 volumes per one volume of the catalyst per hour.
6. A method according to any one preceding claim, wherein the circulation ratio of the hydrogen-containing gas to the liquid feed with the recycle is from 600 to 2,000 nl/l.
7. A method according to any one preceding claim, wherein the hydrogen-containing gas contains at least 50% by volume of hydrogen.
8. A method according to any one preceding claim, wherein the recovered benzene is purified from non-aromatic hydrocarbon impurities.
9. A method according to any one of Claims 1 to 7, wherein the recovered benzene is mixed with the low-boiling fraction of the reforming catalysate and pure benzene is isolated from said mixture.
10. A method according to any one preceding claim, wherein the H-mordenite contains alkali-earth and/or rare-earth metals in an amount equivalent to a degree of substitution of the hydrogen in H-mordenite of up to 50%.
11. A method according to any one preceding claim, wherein the hydrogenating component contains Mo or W in the oxide or sulphide form or Pt, Co, or Ni in the elemental or sulphide form.
12. A method according to any one preceding claim, wherein the binder is alumina.
13. A method according to Claim 1 substantially as hereinbefore disclosed.
14. A method of preparing benzene and xylenes substantially as described in Examples 1 to 9 set forth hereinbefore.
15. Benzene and/or xylenes whenever prepared by a method according to any one preceding claim.

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